

101538, 998 Yang chu 12-27-2006

Connecting via Winsock to STN

cloast prior art 2/3

Welcome to STN International! Enter x:x

LOGINID: ssptaylc1626

PASSWORD :

TERMINAL (ENTER 1, 2, 3, OR ?):2

* * * * * * * * * * * * * Welcome to STN International * * * * * * * * * * * * * *

NEWS 1 Web Page URLs for STN Seminar Schedule - N. America
NEWS 2 "Ask CAS" for self-help around the clock
NEWS 3 AUG 09 INSPEC enhanced with 1898-1968 archive
NEWS 4 AUG 28 ADISCTI Reloaded and Enhanced
NEWS 5 AUG 30 CA(SM)/CAplus(SM) Austrian patent law changes
NEWS 6 SEP 21 CA/CAplus fields enhanced with simultaneous left and right truncation
NEWS 7 SEP 25 CA(SM)/CAplus(SM) display of CA Lexicon enhanced
NEWS 8 SEP 25 CAS REGISTRY(SM) no longer includes Concord 3D coordinates
NEWS 9 SEP 25 CAS REGISTRY(SM) updated with amino acid codes for pyrrolysine
NEWS 10 SEP 28 CEABA-VTB classification code fields reloaded with new classification scheme
NEWS 11 OCT 19 LOGOFF HOLD duration extended to 120 minutes
NEWS 12 OCT 19 E-mail format enhanced
NEWS 13 OCT 23 Option to turn off MARPAT highlighting enhancements available
NEWS 14 OCT 23 CAS Registry Number crossover limit increased to 300,000 in multiple databases
NEWS 15 OCT 23 The Derwent World Patents Index suite of databases on STN has been enhanced and reloaded
NEWS 16 OCT 30 CHEMLIST enhanced with new search and display field
NEWS 17 NOV 03 JAPIO enhanced with IPC 8 features and functionality
NEWS 18 NOV 10 CA/CAplus F-Term thesaurus enhanced
NEWS 19 NOV 10 STN Express with Discover! free maintenance release Version 8.01c now available
NEWS 20 NOV 20 CAS Registry Number crossover limit increased to 300,000 in additional databases
NEWS 21 NOV 20 CA/CAplus to MARPAT accession number crossover limit increased to 50,000
NEWS 22 DEC 01 CAS REGISTRY updated with new ambiguity codes
NEWS 23 DEC 11 CAS REGISTRY chemical nomenclature enhanced
NEWS 24 DEC 14 WPIDS/WPINDEX/WPIX manual codes updated
NEWS 25 DEC 14 GBFULL and FRFULL enhanced with IPC 8 features and functionality
NEWS 26 DEC 18 CA/CAplus pre-1967 chemical substance index entries enhanced with preparation role
NEWS 27 DEC 18 CA/CAplus patent kind codes updated
NEWS 28 DEC 18 MARPAT to CA/CAplus accession number crossover limit increased to 50,000
NEWS 29 DEC 18 MEDLINE updated in preparation for 2007 reload
NEWS 30 DEC 27 CA/CAplus enhanced with more pre-1907 records

NEWS EXPRESS NOVEMBER 10 CURRENT WINDOWS VERSION IS V8.01C, CURRENT MACINTOSH VERSION IS V6.0C(ENG) AND V6.0JC(JP), AND CURRENT DISCOVER FILE IS DATED 25 SEPTEMBER 2006.

NEWS HOURS STN Operating Hours Plus Help Desk Availability
NEWS LOGIN Welcome Banner and News Items
NEWS IPC8 For general information regarding STN implementation of IPC 8

NEWS X25 X.25 communication option no longer available
NEWS PRICE STN 2007 Prices

Enter NEWS followed by the item number or name to see news on that specific topic.

All use of STN is subject to the provisions of the STN Customer agreement. Please note that this agreement limits use to scientific research. Use for software development or design or implementation of commercial gateways or other similar uses is prohibited and may result in loss of user privileges and other penalties.

FILE 'HOME' ENTERED AT 14:54:20 ON 27 DEC 2006

FILE 'REGISTRY' ENTERED AT 14:54:37 ON 27 DEC 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2006 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6
DICTIONARY FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH June 30, 2006

Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=> Uploading C:\Documents and Settings\ychu\Desktop\Case\10538998\10638998B.str

L1 STRUCTURE UPLOADED

=> d
L1 HAS NO ANSWERS
L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> S 11
SAMPLE SEARCH INITIATED 14:55:46 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 36 TO ITERATE

100.0% PROCESSED 36 ITERATIONS 18 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 360 TO 1080
PROJECTED ANSWERS: 106 TO 614

L2 18 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 14:56:07 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 634 TO ITERATE

100.0% PROCESSED 634 ITERATIONS 400 ANSWERS
SEARCH TIME: 00.00.01

L3 400 SEA SSS FUL L1

=> file caplus
COST IN U.S. DOLLARS SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST 167.82 168.03

FILE 'CAPLUS' ENTERED AT 14:56:21 ON 27 DEC 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2006 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 27 Dec 2006 VOL 146 ISS 1
FILE LAST UPDATED: 26 Dec 2006 (20061226/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply.
They are available for your review at:

<http://www.cas.org/infopolicy.html>

=> s l3
L4 1 L3

=> d ibib abs tot

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:589417 CAPLUS
DOCUMENT NUMBER: 141:140320
TITLE: A preparation of insecticidal piperidine and pyridine derivatives
INVENTOR(S): Ding, Ping; Henrie, Robert H.; II; Cohen, Daniel H.; Lyga, John W.; Rosen, David S.; Theodoridis, George; Zhang, Qun; Yeager, Walter H.; Donovan, Stephen F.; Zhang, Steven Shunxiang; Shulman, Inna; Yu, Seong Jae; Wang, Guozhi; Zhang, Y. Larry; Gopalsamy, Ariamala; Warkentin, Dennis L.; Rensner, Paul E.; Silverman, Ian

PATENT ASSIGNEE(S): R.; Cullen, Thomas G.
 FMC Corporation, USA
 SOURCE: PCT Int. Appl., 182 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|------------------|------------|
| WO 2004060371 | A1 | 20040722 | WO 2003-US38878 | 20031208 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,
TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2003296308 | A1 | 20040729 | AU 2003-296308 | 20031208 |
| EP 1572207 | A1 | 20050914 | EP 2003-814662 | 20031208 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK | | | | |
| BR 2003017324 | A | 20051116 | BR 2003-17324 | 20031208 |
| CN 1729178 | A | 20060201 | CN 2003-80106750 | 20031208 |
| CN 1744895 | A | 20060308 | CN 2003-80109445 | 20031208 |
| JP 2006516149 | T | 20060622 | JP 2005-508561 | 20031208 |
| US 2006135504 | A1 | 20060622 | US 2005-538998 | 20051216 |
| PRIORITY APPLN. INFO.: | | | US 2002-434718P | P 20021218 |
| | | | US 2003-495059P | P 20030814 |
| | | | WO 2003-US38878 | W 20031208 |

OTHER SOURCE(S): MARPAT 141:140320
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to a prepn. of insecticidal piperidine and pyridine derivs. of formula I [wherein: A is C or CH; B is substituted phenyl; C is O-1; D is (CH₂)₀₋₃; E is a bridging group selected from (CR₉R₁₀)-(CR₁₁R₁₂)₀₋₁, (CR₉R₁₀)-(CR₁₁R₁₂)₀₋₁₀, C₃H₆, C(O), or C(S)NH, etc.; R₁ is H, alkyl, alkoxyalkyl, or aryl; R₂, R₃, R₄, R₅, and R₆ are independently selected from H, halogen, (halo/hydroxy)alkyl, alkylthio, CN, or NO₂, etc.; R₇ is (halo/hydroxy/alkoxy/dialkylamino)alkyl, sulfonatoalkyl, arylalkyl, or arylcarbonyl, etc.; R₈ is H, (cyclo)alkyl, alkoxy, amino, morpholinyl, or indolyl, etc.; R₉, R₁₀, R₁₁, and R₁₂ are independently selected from H, alkyl, aryl, etc.]. Prepd. compds. were evaluated for activity against tobacco budworm in a surface-treated diet test. For instance, piperidine deriv. II (compd. 101, insecticidal activity: 100% mortality, 100% growth inhibition) was prep'd. via elimination reaction of hydroxymethylpiperidine deriv. III, N-benzylation of the obtained methylenepiperidine deriv. IV by 4-nitrophenylmethyl bromide, subsequent redn. of the nitro-group, N-carboxylation of the obtained amine V, and N-oxidn. (example 1).

=> file reg
COST IN U.S. DOLLARS

SINCE FILE
ENTRY

TOTAL
SESSION

| | | |
|--|------------------|---------------|
| FULL ESTIMATED COST | 3.66 | 171.69 |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | SINCE FILE ENTRY | TOTAL SESSION |
| CA SUBSCRIBER PRICE | -0.75 | -0.75 |

FILE 'REGISTRY' ENTERED AT 14:57:29 ON 27 DEC 2006
 USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
 PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
 COPYRIGHT (C) 2006 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6
 DICTIONARY FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH June 30, 2006

Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=>
 Uploading C:\Documents and Settings\ychu\Desktop\Case\10538998\10638998B-1.str

L5 STRUCTURE uploaded

=> d
 L5 HAS NO ANSWERS
 L5 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> s 15
 SAMPLE SEARCH INITIATED 14:57:53 FILE 'REGISTRY'
 SAMPLE SCREEN SEARCH COMPLETED - 490 TO ITERATE

100.0% PROCESSED 490 ITERATIONS 1 ANSWERS
 SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
 BATCH **COMPLETE**
 PROJECTED ITERATIONS: 8472 TO 11128
 PROJECTED ANSWERS: 1 TO 80

L6 1 SEA SSS SAM L5

=> s 15 full
 FULL SEARCH INITIATED 14:58:00 FILE 'REGISTRY'
 FULL SCREEN SEARCH COMPLETED - 9892 TO ITERATE

100.0% PROCESSED 9892 ITERATIONS 14 ANSWERS

SEARCH TIME: 00.00.01

L7 14 SEA SSS FUL L5

| | | | |
|--|------------------|---------------|--|
| => file caplus | | | |
| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION | |
| FULL ESTIMATED COST | 166.94 | 338.63 | |
| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | SINCE FILE ENTRY | TOTAL SESSION | |
| CA SUBSCRIBER PRICE | 0.00 | -0.75 | |

FILE 'CAPLUS' ENTERED AT 14:58:09 ON 27 DEC 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2006 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 27 Dec 2006 VOL 146 ISS 1
FILE LAST UPDATED: 26 Dec 2006 (20061226/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

<http://www.cas.org/infopolicy.html>

=> s 17
L8 3 L7

=>.d ibib abs tot

L8 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:589417 CAPLUS
DOCUMENT NUMBER: 141:140320
TITLE: A preparation of insecticidal piperidine and pyridine derivatives
INVENTOR(S): Ding, Ping; Henrie, Robert H., II; Cohen, Daniel H.; Lyga, John W.; Rosen, David S.; Theodoridis, George; Zhang, Qun; Yeager, Walter H.; Donovan, Stephen F.; Zhang, Steven Shunxiang; Shulman, Inna; Yu, Seong Jae; Wang, Guozhi; Zhang, Y. Larry; Gopalsamy, Ariamala; Warkentin, Dennis L.; Rensner, Paul E.; Silverman, Ian R.; Cullen, Thomas G.
PATENT ASSIGNEE(S): FMC Corporation, USA
SOURCE: PCT Int. Appl., 182 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|-------|-------|-----------------|-------|
| ----- | ----- | ----- | ----- | ----- |

| | | | | |
|--|----|----------|------------------|------------|
| WO 2004060371 | A1 | 20040722 | WO 2003-US38878 | 20031208 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,
TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2003296308 | A1 | 20040729 | AU 2003-296308 | 20031208 |
| EP 1572207 | A1 | 20050914 | EP 2003-814662 | 20031208 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK | | | | |
| BR 2003017324 | A | 20051116 | BR 2003-17324 | 20031208 |
| CN 1729178 | A | 20060201 | CN 2003-80106750 | 20031208 |
| CN 1744895 | A | 20060308 | CN 2003-80109445 | 20031208 |
| JP 2006516149 | T | 20060622 | JP 2005-508561 | 20031208 |
| US 2006135504 | A1 | 20060622 | US 2005-538998 | 20051216 |
| PRIORITY APPLN. INFO.: | | | US 2002-434718P | P 20021218 |
| | | | US 2003-495059P | P 20030814 |
| | | | WO 2003-US38878 | W 20031208 |

OTHER SOURCE(S): MARPAT 141:140320

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to a prepn. of insecticidal piperidine and pyridine derivs. of formula I [wherein: A is C or CH; B is substituted phenyl; C is O-1; D is (CH₂)₀₋₃; E is a bridging group selected from (CR₉R₁₀)-(CR₁₁R₁₂)₀₋₁, (CR₉R₁₀)-(CR₁₁R₁₂)₀₋₁₀, C₃H₆, C(O), or C(S)NH, etc.; R₁ is H, alkyl, alkoxyalkyl, or aryl; R₂, R₃, R₄, R₅, and R₆ are independently selected from H, halogen, (halo/hydroxy)alkyl, alkylthio, CN, or NO₂, etc.; R₇ is (halo/hydroxy/alkoxy/dialkylamino)alkyl, sulfonatoalkyl, arylalkyl, or arylcarbonyl, etc.; R₈ is H, (cyclo)alkyl, alkoxy, amino, morpholinyl, or indolyl, etc.; R₉, R₁₀, R₁₁, and R₁₂ are independently selected from H, alkyl, aryl, etc.]. Prepd. compds. were evaluated for activity against tobacco budworm in a surface-treated diet test. For instance, piperidine deriv. II (compd. 101, insecticidal activity: 100% mortality, 100% growth inhibition) was prepd. via elimination reaction of hydroxymethylpiperidine deriv. III, N-benzylation of the obtained methylenepiperidine deriv. IV by 4-nitrophenylmethyl bromide, subsequent redn. of the nitro-group, N-carboxylation of the obtained amine V, and N-oxidn. (example 1).

L8 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1964:16612 CAPLUS

DOCUMENT NUMBER: 60:16612

ORIGINAL REFERENCE NO.: 60:2903b-h

TITLE: Phenyl(pyridyl or piperidyl)alkyl benzoates and phenylalkanoates

INVENTOR(S): Rorig, Kurt J.

PATENT ASSIGNEE(S): G.D. Searle and Co.

SOURCE: 10 pp.

DOCUMENT TYPE: Patent

LANGUAGE: Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.

KIND DATE

APPLICATION NO.

DATE

US 3100775 19630813 US 1959-803371 19590401
 PRIORITY APPLN. INFO.: , US 19590401
 GI For diagram(s), see printed CA Issue.
 AB Carbinols of the general formula RR'ArCR''nOH, where R is an alkyl or aryl group, R' is a pyridyl or piperidyl group, Ar is an aryl group, R'' is an alkylene group, and n is 0 or 1, are treated with anhydrides of the general formula (PhRnCO)2O, where R is an alkylene group and n is 0 or 1, to give the title compds. which can be used as spasmolytic and fungicidal agents. Thus, a mixt. of .alpha.-phenyl-4-pyridinemethanol 25 and o-C1C6H4COCl 60 parts is heated 11 hrs. under N at 130-50.degree., cooled to .apprx.30.degree., treated with excess 10% NaOH, and extd. with ether. The ether ext. is extd. with dil. HCl, the acid ext. made alk. with NaOH, the ppt. sepd. and taken up in ether, the ether mixt. filtered, dried, and evapd., and the residue obtained distd. in vacuo to give .alpha.-phenyl-4-pyridylmethyl o-chlorobenzoate, b0.15 175-95.degree.. Similarly prep'd. are the following I (m, n, R, R1, R2, R3, X, X1, X2, X3, X4, m.p., and m.p. HCl salt given): 0, 0, 4-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.68-9.degree. (petr. ether), --; 0, 0, 2-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.76-7.degree. (petr. ether), --; 0, 0, 4-pyridyl, H, H, H, H, Cl, Cl, Cl, H, --, 205-7.degree. (EtOH-ether); 0, 0, 4-pyridyl, H, H, H, MeO, H, H, H, H, --(b0.8 180-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, MeO, H, H, 94-6.degree. (b0.3 185-205.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, EtO, H, H, 96-9.degree. (b0.3 195-200.degree.), --; 0, 1, 4-pyridyl, H, H, H, H, MeO, H, H, --(b0.4 185-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, H, --, 210-12.degree.; 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, 118-20.degree., .apprx.219-20.degree. (EtOH-anhyd. ether) (maleate m. 117-19.degree.); 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, MeO, H, MeO, H, --, 202-4.degree.; 0, 0, 2-pyridyl, H, H, H, H, MeO, MeO, MeO, H, 115-16.degree. (iso-PrOH), 172.5-4.degree. (EtOH-ether); 0, 0, 3-pyridyl, H, H, H, MeO, MeO, H, --, 192-4.degree. (EtOH); 1, 0, 4-pyridyl, H, H, H, MeO, MeO, H, --, --; 0, 1, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 182.degree.; 0, 2, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 4-pyridyl, H, Me, H, H, MeO, MeO, MeO, H, --, 200-2.degree. (abs. EtOH-ether); 0, 0, 4-pyridyl, H, Me, H, H, EtO, EtO, EtO, H, --, 207-10.degree. (abs. EtOH); 0, 0, 4-pyridyl, H, H, Et, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-pyridyl, H, Cl, H, H, MeO, MeO, H, --, 204-6.degree. (abs. EtOH); 0, 0, 4-pyridyl, Cl, H, H, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-piperidyl, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-methyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-octyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-benzyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, -- [HBr salt m. 227-30.degree. (abs. EtOH-ether)]; 0, 0, 4-pyridyl, H, H, H, CO2H, H, H, H, H, .apprx.201-2.degree., --; 0, 0, 4-pyridyl, H, H, H, CO2Me, H, H, H, H, --, 96-9.degree.; 0, 0, 4-pyridyl, H, H, H, H, CO2Et, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, NO2, H, H, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, H, NMe2, H, H, H, --(b0.2 200-10.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, NET2, H, H, --, --. Also prep'd. were the following (m.p. and m.p. HCl salt given): .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxycinnamate, --, 200-1.degree.; .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate N-oxide, --, --(.lambda. 6.72 .mu.); 4-pyridinemethyl 3,3,5-trimethoxybenzoate, --, 210-11.degree. (EtOH); .alpha., .alpha.-diphenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate, 160.5-1.5.degree. (iso-PrOH), --. Also prep'd. are (m.p. given): (3,4,5-C13C6H2CO)2O, 206-10.degree.; .alpha.-m-tolyl-4-pyridinemethanol, 147-50.degree. (C6H6); .alpha.-m-chlorophenyl-4-pyridinemethanol, 133-5.degree.; .alpha.-phenyl-4-piperidinemethanol, 168-9.degree. (abs. EtOH); 4-benzoyl-1-methylpyridinium iodide, --; 1-methyl-.alpha.-phenyl-4-piperidinemethanol, --; 4-benzoyl-1-benzylpyridinium chloride, .apprx.193-4.degree. (butanone); 1-benzyl-.alpha.-phenyl-4-

piperidinemethanol-HCl, 190-3.degree. (abs. EtOH-anhyd. ether).

L8 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1954:28787 CAPLUS
DOCUMENT NUMBER: 48:28787
ORIGINAL REFERENCE NO.: 48:5189d-i,5190a-i,5191a-c
TITLE: Quinolyl ketones. I
AUTHOR(S): de Diesbach, Henri; Pugin, Andre; Morard, Francois;
Nowaczinski, Wojciech; Dessibourg, Joseph
CORPORATE SOURCE: Univ. Fribourg, Switz.
SOURCE: Helvetica Chimica Acta (1952), 35, 2322-32
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: French
OTHER SOURCE(S): CASREACT 48:28787
GI For diagram(s), see printed CA Issue.
AB A no. of quinolyl ketones (I), prep'd. by the Skraup synthesis from 4-aminobenzophenones, have been reduced with Raney Ni and H at ordinary pressure and temp. to the tetrahydro derivs. (II) and with (iso-PrO)3Al to the carbinols (III), but could not be reduced to the tetrahydro carbinols (IV.). Raney Ni reduces III to the methylene derivs. (V) instead of to IV. Thus 6-benzoylquinoline (VI), colorless crystals, m. 60.5.degree. (from ligroine) [VI.H2O, white plates, m. 39-40.degree. (from MeOH or EtOH); picrate, m. 222.degree.; phenylhydrazone, m. 184.degree.; syn-oxime, m. 198-205.degree.; anti-oxime, m. 192-5.degree.], is prep'd. by heating p-H2NC6H4Bz, PhNO2, glycerol, and concd. H2SO4 3 h. at 160.degree., dilg., treating with steam, acidifying, alkalizing, taking up in Et2O, filtering, and distg. at 240.degree./16 mm. Similarly are prep'd. the following compds. [(a) starting amine, and (b) corresponding quinoline deriv.]: (a) 3,4-Me(H2N)C6H3Bz; (b) 6-benzoyl-8-methylquinoline. (VII), yellowish plates, m. 199.degree. (from AcOH) [phenylhydrazone, m. 235-7.degree. (from C6H6)]. (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(p-chlorobenzoyl)quinoline (VIII), m. 204.degree. (from ligroine, b. 120-80.degree., then from MeOH). (a) 4-Amino-2',4'-dichlorobenzophenone, m. 130-1.degree. (100% yield by Raney Ni hydrogenation of the 4-nitro analog in MeOH 24 h. at 100.degree. and 80 atm.); (b) 6-(2,4-dichlorobenzoyl)quinoline (IX), white crystals, m. 131-2.degree.. (a) 4-Amino-2',5'-dichlorobenzophenone, white crystals, m. 123.degree. (from 60% alc.), from the 4-nitro analog with SnCl2 or Na2S; (b) 6-(2,5-dichlorobenzoyl)quinoline (X), white needles, m. 134-5.degree. (from dil. alc.) (picrate, m. 208-9.degree.). (a) 4-Amino-3',4'-dichlorobenzophenone, white crystals, m. 161-2.degree. (from alc.), from the 4-nitro compd. with SnCl2; (b) 6-(3,4-dichlorobenzoyl)quinoline (XI), m. 139-40.degree. (from ligroine and MeOH) (picrate, m. 173-4.degree.). (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(4-chlorobenzyl)quinoline, m. 191.5-2.degree. (from alc.). (a) 4-Amino-2',4'-dichlorodiphenylmethane, blue crystals, m. 102-3.degree. (Ac deriv., m. 141-2.degree.), from the 4-nitro compd. with SnCl2; (b) 6-(2,4-dichlorobenzyl)quinoline (in poor yield) (picrate, m. 167-8.degree.). (a) 4-Amino-3',4'-dichlorodiphenylmethane, an oil (Bz deriv., m. 106-7.degree.), from the 4-nitro compd. and SnCl2; (b) 6-(3,4-dichlorobenzyl)quinoline (picrate, m. 164-5.degree.). 6-Acetyl-1,2,3,4-tetrahydroquinoline (XII), greenish plates, m. 105-7.degree. (picrate, m. 125.degree.; oxime, m. 144.degree.), is prep'd. by condensing 1-acetyl-1,2,3,4-tetrahydroquinoline with ClCH2COCl at room temp., sapong. the 1-Ac group with boiling 20% HCl, and heating in 80% alc. with powd. Fe and 2N HCl; heated 5 h. at 188.degree. in a sealed tube with Hg(OAc)2, AcOH, and H2O it gives yellowish prisms of 6-acetylquinoline, m. 75-6.degree. (picrate, m. 242.degree.). A Beckmann rearrangement of XII oxime gives 6-amino-1,2,3,4-tetrahydroquinoline, m. 95.5-6.degree.. Na redn. of Quinaldine in AmOH gives 93% 1,2,3,4-tetrahydroquininaldine, acetylated with Ac2O to the 1-Ac deriv., b12 153.degree., yellow crystals, m. 57.degree.; which, treated with ClCH2COCl in CS2, then slowly with AlCl3, and let stand 2 days yields 6-(chloroacetyl)-1,2,3,4-tetrahydroquininaldine-HCl, white crystals, m.

225-6.degree., converted by neutralization with dil. alkali to the free quinaldine, yellow crystals, m. 121.degree., which is dechlorinated in 80% HCl with Fe and 2N HCl to 6-acetyl-1,2,3,4-tetrahydroquininaldine, m. 69.degree.. The following 1,2,3,4-tetrahydroquinolines are prep'd. in good yield by hydrogenating 5 g. of the appropriate I in 50 mL. MeOH at room temp. and pressure in the presence of Raney Ni, warming, filtering, washing the Ni with warm MeOH, evapg. to a small vol., and recrystg.: 6-benzoyl (XIII), yellowish crystals, m. 113.degree. [1-ON deriv., m. 119-20.degree.; 1-Bz deriv., m. 131.degree. (from 50% AcOH); 1-Ac deriv., m. 97.degree. (from dil. alc.)]; 6-benzoyl-8-Me, pale yellow needles, m. 118.degree.; 6-(p-chlorobenzoyl)tetrahydroquinoline, m. 156.degree. (1-ON deriv., m. 173-4.degree.; 6-Bz deriv., m. 146.degree.); 6-(2,4-dichlorobenzoyl), m. 137.degree. (1-ON deriv., m. 145.degree.); 6-(2,5-dichlorobenzoyl), m. 153.degree.. The Meerwein-Ponndorf redn. of I to III is carried out in nearly 100% yield by adding 10 g. of the I in 30 mL. iso-PrOH to (iso-PrO)₃Al (made by refluxing 2.5 g. Al paste 10 h. with 0.125 g. HgCl₂ in 50 mL. abs. iso-PrOH), slowly distg. the Me₂CO formed, alkalizing, steam-distg. the iso-PrOH, adding boiling H₂O to the residue, and crystg. from dil. alc. Thus are prep'd. the following carbinols: phenyl(6-quinolyl) (XIV), m. 127-8.degree. (picrate, m. 190.degree.; picrate of the acetate (ester), m. 188.degree.); phenyl(8-methyl-6-quinolyl) (XV), m. 133.degree. [picrate, m. 202-3.degree.; acetate (ester), m. 100.degree. (from dil. alc.)]; (p-chlorophenyl)(6-quinolyl), m. 153.degree. (picrate, m. 186.degree.; picrate of the acetate (ester), m. 209.degree.); (2,4-dichlorophenyl)(6-quinolyl), m. 161.degree. (picrate, m. 225.degree.; acetate (ester), m. 125-6.degree.; picrate of the acetate, m. 212.degree.); X, (2, 5-dichlorophenyl)(6-quinolyl), m. 161.degree. (acetate (ester), m. 174.degree.); (3,4-dichlorophenyl)(6-quinolyl), m. 145.degree. (picrate of the acetate (ester), m. 189-90.degree.). Raney Ni hydrogenation of XIV gives 6-benzylquinoline, white crystals, m. 48-9.degree.; similarly XV is reduced to 6-benzyl-8-methylquinoline, m. 55.degree.. An attempted (iso-PrO)₃Al redn. of XIII to the corresponding IV gives instead a white paste, m. 120-40.degree., sol. in C₆H₆ and CHCl₃, slightly sol. in alc. 2-Benzoylquinoline is reduced by (iso-PrO)₃Al in 100% yield to phenyl(2-quinolyl)carbinol (XVI), white crystals, m. 69.degree. (from ligroine); also obtained by Raney Ni hydrogenation at room pressure and temp. [picrate, yellow crystals, m. 138.degree. (from alc.)], instead of to the tetrahydro deriv. Phenyl(1,2,3,4-tetrahydro-2-quinolyl)carbinol, b0.005 140.degree. [1-ON deriv., yellow plates, m. 103.degree. (from dil. alc.); N,O-di-Bz deriv., m. 161.degree. (from ligroine)], is prep'd. by reducing 2 g. 2-benzoylquinoline 1 h. in 300 g. MeOH with H at 70.degree. and 50 atm. in the presence of Raney Ni, filtering, washing with MeOH, evapg. to a small vol., dilg. with H₂O, adding Et₂O, and vacuum-distg. the oil. 4-Benzoylquinoline is reduced by (iso-PrO)₃Al to phenyl(4-quinolyl)carbinol, m. 127.degree. (from dil. alc.) (acetate (ester), white plates, m. 100.degree.), and by Raney Ni hydrogenation at 100.degree. and 70 atm. to phenyl(1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 135.degree. (from dil. alc.), b0.001 110-15.degree. [1-ON deriv., yellow leaves, m. 105.degree. (from dil. alc.); N,O-di-Bz deriv., m. 156.degree. (from ligroine)]. 2-Methyl-4-benzoylquinoline (XVII), bright plates, m. 118.degree. (from ligroine), is prep'd. by heating 2 g. 2-methyl-4-quinoliniccarboxamide in 30 mL. POCl₃ with 3 g. PC15 (with 2 drops water added to start the reaction) 15-20 min. at 110.degree., cooling with ice, neutralizing, extg. with Et₂O, crystg. from ligroine the 2-methyl-4-cyanoquinoline (XVIII), white needles, m. 106.degree., and adding the Grignard reagent from 12 g. PhBr and 2 g. Mg in 30 mL. Et₂O to 5 g. XVIII in 50 mL. Et₂O; XVII is reduced by (iso-PrO)₃Al to phenyl(2-methyl-4-quinolyl)carbinol, colorless prisms, m. 167.degree. (from dil. alc.) [acetate (ester), m. 103.degree. (from dil. alc.)], and by Raney Ni hydrogenation at 100.degree. and 70 atm. to phenyl(2-methyl-1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 162.degree. (from dil. alc.), b0.001 130.degree. [N,O-Bz deriv., m. 149.degree. (from ligroine)]. Raney Ni redn. at room pressure and temp. of

8-benzoylquinoline gives at once phenyl(1,2,3,4-tetrahydro-8-quinolyl)carbinol, oil, b0.001 120.degree. [1-ON deriv., yellow prisms, m. 146.degree. (from alc.), (di-Bz deriv., m. 132.degree. (from ligroine)]. Nitration of 6 g. VI in 25 mL. concd. H₂SO₄ with 1 mL. nitrating mixt. (= 0.255 g. HNO₃) added at -10.degree., followed by cooling with ice, filtering, neutralizing with NH₄OH, and crystg. in alc., gives 6-(m-nitrobenzoyl)quinoline, yellow needles, m. 160.degree., which reduced by SnCl₂ in alc. to the amino compd., yellow crystals, m. 142.degree. (from H₂O). Similarly, VII is nitrated to 6-(m-nitrobenzoyl)-8-methylquinoline, m. 156.degree., which is reduced to the 3-amino compd., yellow crystals, m. 187.degree. (from ligroine). The (dichlorobenzoyl)quinolines cannot be nitrated.

=> d ibib abs hitstr 2-3

L8 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1964:16612 CAPLUS
 DOCUMENT NUMBER: 60:16612
 ORIGINAL REFERENCE NO.: 60:2903b-h
 TITLE: Phenyl(pyridyl or piperidyl)alkyl benzoates and phenylalkanoates
 INVENTOR(S): Rorig, Kurt J.
 PATENT ASSIGNEE(S): G.D. Searle and Co.
 SOURCE: 10 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

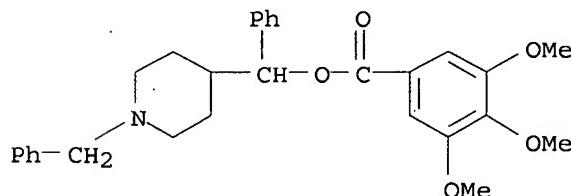
do not prior art

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|-------|----------|-----------------|----------|
| US 3100775 | ----- | 19630813 | US 1959-803371 | 19590401 |
| PRIORITY APPLN. INFO.: | | | US | 19590401 |

GI For diagram(s), see printed CA Issue.
 AB Carbinols of the general formula RR'ArCR''NOH, where R is an alkyl or aryl group, R' is a pyridyl or piperidyl group, Ar is an aryl group, R'' is an alkylene group, and n is 0 or 1, are treated with anhydrides of the general formula (PhRnCO)₂O, where R is an alkylene group and n is 0 or 1, to give the title compds. which can be used as spasmolytic and fungicidal agents. Thus, a mixt. of .alpha.-phenyl-4-pyridinemethanol 25 and o-ClC₆H₄COCl 60 parts is heated 11 hrs. under N at 130-50.degree., cooled to .apprx.30.degree., treated with excess 10% NaOH, and extd. with ether. The ether ext. is extd. with dil. HCl, the acid ext. made alk. with NaOH, the ppt. sepd. and taken up in ether, the ether mixt. filtered, dried, and evapd., and the residue obtained distd. in vacuo to give .alpha.-phenyl-4-pyridylmethyl o-chlorobenzoate, b0.15 175-95.degree.. Similarly prep'd. are the following I (m, n, R, R₁, R₂, R₃, X, X₁, X₂, X₃, X₄, m.p., and m.p. HCl salt given): 0, 0, 4-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.68-9.degree. (petr. ether), --; 0, 0, 2-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.76-7.degree. (petr. ether), --; 0, 0, 4-pyridyl, H, H, H, H, Cl, Cl, Cl, H, --, 205-7.degree. (EtOH-ether); 0, 0, 4-pyridyl, H, H, H, MeO, H, H, H, H, --(b0.8 180-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, MeO, H, H, 94-6.degree. (b0.3 185-205.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, EtO, H, H, 96-9.degree. (b0.3 195-200.degree.), --; 0, 1, 4-pyridyl, H, H, H, H, MeO, H, H, --(b0.4 185-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, H, H, --, 210-12.degree.; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, H, H, 118-20.degree., .apprx.219-20.degree. (EtOH-anhyd. ether) (maleate m. 117-19.degree.); 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, MeO, MeO, H, H, --, 202-4.degree.; 0, 0, 2-pyridyl, H, H, H, H, MeO, MeO, MeO, H, H, 115-16.degree. (iso-PROH), 172.5-4.degree. (EtOH-ether); 0, 0, 3-pyridyl, H, H, H, H, MeO, MeO, H, H, --, 192-4.degree. (EtOH); 1, 0, 4-pyridyl,

H, H, H, H, MeO, MeO, H, --, --; 2, 0, 4-pyridyl, H, H, H, H, MeO,
 MeO, MeO, H, --, --; 0, 1, 4-pyridyl, H, H, H, MeO, MeO, MeO, H, --,
 182.degree.; 0, 2, 4-pyridyl, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0,
 4-pyridyl, H, Me, H, H, MeO, MeO, MeO, H, --, 200-2.degree. (abs.
 EtOH-ether); 0, 0, 4-pyridyl, H, Me, H, H, EtO, EtO, EtO, H, --,
 207-10.degree. (abs. EtOH); 0, 0, 4-pyridyl, H, H, Et, H, EtO, EtO, EtO,
 H, --, --; 0, 0, 4-pyridyl, H, Cl, H, H, MeO, MeO, MeO, H, --,
 204-6.degree. (abs. EtOH); 0, 0, 4-pyridyl, Cl, H, H, H, EtO, EtO, EtO, H,
 --, --; 0, 0, 4-piperidyl, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0,
 1-methyl-4-piperidyl, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0,
 1-octyl-4-piperidyl, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0,
 1-benzyl-4-piperidyl, H, H, H, MeO, MeO, MeO, H, --, -- [HBr salt m.
 227-30.degree. (abs. EtOH-ether)]; 0, 0, 4-pyridyl, H, H, H, CO2H, H, H,
 H, H, .apprx.201-2.degree., --; 0, 0, 4-pyridyl, H, H, H, CO2Me, H, H, H,
 H, --, 96-9.degree.; 0, 0, 4-pyridyl, H, H, H, H, CO2Et, H, H, --, --,
 0, 0, 4-pyridyl, H, H, H, NO2, H, H, H, --, --; 0, 0, 4-pyridyl, H, H,
 H, H, NO2, H, H, --, 224-7.degree.; 0, 0, 4-pyridyl, H, H, H, NMe2,
 H, H, H, --(b0.2 200-10.degree.), --; 0, 0, 4-pyridyl, H, H, H, H,
 NET2, H, H, --, --. Also prep'd. were the following (m.p. and m.p. HCl
 salt given): .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxycinnamate,
 --, 200-1.degree.; .alpha.-phenyl-4-pyridinemethyl 3,4,5-
 trimethoxybenzoate N-oxide, --, --(.lambda. 6.72 .mu.); 4-pyridinemethyl
 3,3,5-trimethoxybenzoate, --, 210-11.degree. (EtOH); .alpha..alpha.-
 diphenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate, 160.5-1.5.degree.
 (iso-PrOH), --. Also prep'd. are (m.p. given): (3,4,5-Cl3C6H2CO)2O,
 206-10.degree.; .alpha.-m-tolyl-4-pyridinemethanol, 147-50.degree. (C6H6);
 .alpha.-m-chlorophenyl-4-pyridinemethanol, 133-5.degree.;
 .alpha.-phenyl-4-piperidinemethanol, 168-9.degree. (abs. EtOH);
 4-benzoyl-1-methylpyridinium iodide, --; 1-methyl-.alpha.-
 phenyl-4-piperidinemethanol, --; 4-benzoyl-1-benzylpyridinium chloride,
 .apprx.193-4.degree. (butanone); 1-benzyl-.alpha.-phenyl-4-
 piperidinemethanol-HCl, 190-3.degree. (abs. EtOH-anhyd. ether).
 IT 98023-55-3P, 4-Piperidinemethanol, 1-benzyl-.alpha.-phenyl-,
 3,4,5-trimethoxybenzoate, hydrobromide
 RL: PREP (Preparation)
 (prep'n. of)

RN 98023-55-3 CAPLUS
 CN Benzoic acid, 3,4,5-trimethoxy-, .alpha.- (1-benzyl-4-piperidyl)benzyl
 ester, hydrobromide (6CI, 7CI) (CA INDEX NAME)



● HBr

L8 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1954:28787 CAPLUS
 DOCUMENT NUMBER: 48:28787
 ORIGINAL REFERENCE NO.: 48:5189d-i,5190a-i,5191a-c
 TITLE: Quinolyl ketones. I
 AUTHOR(S): de Diesbach, Henri; Pugin, Andre; Morard, Francois;
 Nowaczinski, Wojciech; Dessimbourg, Joseph
 CORPORATE SOURCE: Univ. Fribourg, Switz.
 SOURCE: Helvetica Chimica Acta (1952), 35, 2322-32

DOCUMENT TYPE:

Journal

LANGUAGE:

French

OTHER SOURCE(S):

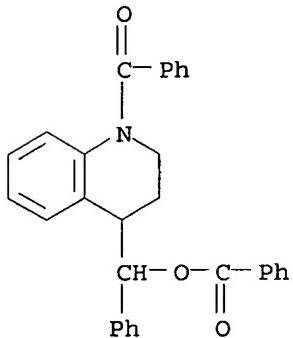
CASREACT 48:28787

GI For diagram(s), see printed CA Issue.

AB A no. of quinolyl ketones (I), prep'd. by the Skraup synthesis from 4-aminobenzophenones, have been reduced with Raney Ni and H at ordinary pressure and temp. to the tetrahydro derivs. (II) and with (iso-PrO)₃Al to the carbinols (III), but could not be reduced to the tetrahydro carbinols (IV.). Raney Ni reduces III to the methylene derivs. (V) instead of to IV. Thus 6-benzoylquinoline (VI), colorless crystals, m. 60.5.degree. (from ligroine) [VI.H₂O, white plates, m. 39-40.degree. (from MeOH or EtOH); picrate, m. 222.degree.; phenylhydrazone, m. 184.degree.; syn-oxime, m. 198-205.degree.; anti-oxime, m. 192-5.degree.], is prep'd. by heating p-H₂NC₆H₄Bz, PhNO₂, glycerol, and concd. H₂SO₄ 3 h. at 160.degree., dilg., treating with steam, acidifying, alkalizing, taking up in Et₂O, filtering, and distg. at 240.degree./16 mm. Similarly are prep'd. the following compds. [(a) starting amine, and (b) corresponding quinoline deriv.]: (a) 3,4-Me(H₂N)C₆H₃Bz; (b) 6-benzoyl-8-methylquinoline. (VII), yellowish plates, m. 199.degree. (from AcOH) [phenylhydrazone, m. 235-7.degree. (from C₆H₆)]. (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(p-chlorobenzoyl)quinoline (VIII), m. 204.degree. (from ligroine, b. 120-80.degree., then from MeOH). (a) 4-Amino-2',4'-dichlorobenzophenone, m. 130-1.degree. (100% yield by Raney Ni hydrogenation of the 4-nitro analog in MeOH 24 h. at 100.degree. and 80 atm.); (b) 6-(2,4-dichlorobenzoyl)quinoline (IX), white crystals, m. 131-2.degree.. (a) 4-Amino-2',5'-dichlorobenzophenone, white crystals, m. 123.degree. (from 60% alc.), from the 4-nitro analog with SnCl₂ or Na₂S; (b) 6-(2,5-dichlorobenzoyl)quinoline (X), white needles, m. 134-5.degree. (from dil. alc.) (picrate, m. 208-9.degree.). (a) 4-Amino-3',4'-dichlorobenzophenone, white crystals, m. 161-2.degree. (from alc.), from the 4-nitro compd. with SnCl₂; (b) 6-(3,4-dichlorobenzoyl)quinoline (XI), m. 139-40.degree. (from ligroine and MeOH) (picrate, m. 173-4.degree.). (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(4-chlorobenzyl)quinoline, m. 191.5-2.degree. (from alc.). (a) 4-Amino-2',4'-dichlorodiphenylmethane, blue crystals, m. 102-3.degree. (Ac deriv., m. 141-2.degree.), from the 4-nitro compd. with SnCl₂; (b) 6-(2,4-dichlorobenzyl)quinoline (in poor yield) (picrate, m. 167-8.degree.). (a) 4-Amino-3',4'-dichlorodiphenylmethane, an oil (Bz deriv., m. 106-7.degree.), from the 4-nitro compd. and SnCl₂; (b) 6-(3,4-dichlorobenzyl)quinoline (picrate, m. 164-5.degree.). 6-Acetyl-1,2,3,4-tetrahydroquinoline (XII), greenish plates, m. 105-7.degree. (picrate, m. 125.degree.; oxime, m. 144.degree.), is prep'd. by condensing 1-acetyl-1,2,3,4-tetrahydroquinoline with ClCH₂COCl at room temp., sapong. the 1-Ac group with boiling 20% HCl, and heating in 80% alc. with powd. Fe and 2N HCl; heated 5 h. at 188.degree. in a sealed tube with Hg(OAc)₂, AcOH, and H₂O it gives yellowish prisms of 6-acetylquinoline, m. 75-6.degree. (picrate, m. 242.degree.). A Beckmann rearrangement of XII oxime gives 6-amino-1,2,3,4-tetrahydroquinoline, m. 95.5-6.degree.. Na redn. of Quinaldine in AmOH gives 93% 1,2,3,4-tetrahydroquinaldine, acetylated with Ac₂O to the 1-Ac deriv., b12 153.degree., yellow crystals, m. 57.degree.; which, treated with ClCH₂COCl in CS₂, then slowly with AlCl₃, and let stand 2 days yields 6-(chloroacetyl)-1,2,3,4-tetrahydroquinaldine-HCl, white crystals, m. 225-6.degree., converted by neutralization with dil. alkali to the free quinaldine, yellow crystals, m. 121.degree., which is dechlorinated in 80% HCl with Fe and 2N HCl to 6-acetyl-1,2,3,4-tetrahydroquinaldine, m. 69.degree.. The following 1,2,3,4-tetrahydroquinolines are prep'd. in good yield by hydrogenating 5 g. of the appropriate I in 50 mL. MeOH at room temp. and pressure in the presence of Raney Ni, warming, filtering, washing the Ni with warm MeOH, evapg. to a small vol., and recrystg.: 6-benzoyl (XIII), yellowish crystals, m. 113.degree. [1-ON deriv., m. 119-20.degree.; 1-Bz deriv., m. 131.degree. (from 50% AcOH); 1-Ac deriv., m. 97.degree. (from dil. alc.)]; 6-benzoyl-8-Me, pale yellow needles, m. 118.degree.; 6-(p-chlorobenzoyl)tetrahydroquinoline, m. 156.degree. (1-ON

deriv., m. 173-4.degree.; 6-Bz deriv., m. 146.degree.);
6-(2,4-dichlorobenzoyl), m. 137.degree. (1-ON deriv., m. 145.degree.);
6-(2,5-dichlorobenzoyl), m. 153.degree.. The Meerwein-Ponndorf redn. of I
to III is carried out in nearly 100% yield by adding 10 g. of the I in 30
mL. iso-PrOH to (iso-PrO)3Al (made by refluxing 2.5 g. Al paste 10 h. with
0.125 g. HgCl₂ in 50 mL. abs. iso-PrOH), slowly distg. the Me₂CO formed,
alkalizing, steam-distg. the iso-PrOH, adding boiling H₂O to the residue,
and crystg. from dil. alc. Thus are prep'd. the following carbinols:
phenyl(6-quinolyl) (XIV), m. 127-8.degree. (picrate, m. 190.degree.);
picrate of the acetate (ester), m. 188.degree.); phenyl(8-methyl-6-
quinolyl) (XV), m. 133.degree. [picrate, m. 202-3.degree.; acetate
(ester), m. 100.degree. (from dil. alc.)]; (p-chlorophenyl)(6-quinolyl),
m. 153.degree. (picrate, m. 186.degree.; picrate of the acetate (ester),
m. 209.degree.); (2,4-dichlorophenyl)(6-quinolyl), m. 161.degree.
(picrate, m. 225.degree.; acetate (ester), m. 125-6.degree.; picrate of
the acetate, m. 212.degree.); X, (2, 5-dichlorophenyl)(6-quinolyl), m.
161.degree. (acetate (ester), m. 174.degree.); (3,4-dichlorophenyl)(6-
quinolyl), m. 145.degree. (picrate of the acetate (ester), m.
189-90.degree.). Raney Ni hydrogenation of XIV gives 6-benzylquinoline,
white crystals, m. 48-9.degree.; similarly XV is reduced to
6-benzyl-8-methylquinoline, m. 55.degree.. An attempted (iso-PrO)3Al
redn. of XIII to the corresponding IV gives instead a white paste, m.
120-40.degree., sol. in C₆H₆ and CHCl₃, slightly sol. in alc.
2-Benzoylquinoline is reduced by (iso-PrO)3Al in 100% yield to
phenyl(2-quinolyl)carbinol (XVI), white crystals, m. 69.degree. (from
ligroine); also obtained by Raney Ni hydrogenation at room pressure and
temp. [picrate, yellow crystals, m. 138.degree. (from alc.)], instead of
to the tetrahydro deriv. Phenyl(1,2,3,4-tetrahydro-2-quinolyl)carbinol,
b0.005 140.degree. [1-ON deriv., yellow plates, m. 103.degree. (from dil.
alc.); N,O-di-Bz deriv., m. 161.degree. (from ligroine)], is prep'd. by
reducing 2 g. 2-benzoylquinoline 1 h. in 300 g. MeOH with H at 70.degree.
and 50 atm. in the presence of Raney Ni, filtering, washing with MeOH,
evapg. to a small vol., dilg. with H₂O, adding Et₂O, and vacuum-distg. the
oil. 4-Benzoylquinoline is reduced by (iso-PrO)3Al to
phenyl(4-quinolyl)carbinol, m. 127.degree. (from dil. alc.) (acetate
(ester), white plates, m. 100.degree.), and by Raney Ni hydrogenation at
100.degree. and 70 atm. to phenyl(1,2,3,4-tetrahydro-4-quinolyl)carbinol,
m. 135.degree. (from dil. alc.), b0.001 110-15.degree. [1-ON deriv.,
yellow leaves, m. 105.degree. (from dil. ac.); N,O-di-Bz deriv., m.
156.degree. (from ligroine)]. 2-Methyl-4-benzoylquinoline (XVII), bright
plates, m. 118.degree. (from ligroine), is prep'd. by heating 2 g.
2-methyl-4-quinolinecarboxamide in 30 mL. POCl₃ with 3 g. PC15 (with 2
drops water added to start the reaction) 15-20 min. at 110.degree.,
cooling with ice, neutralizing, extg. with Et₂O, crystg. from ligroine the
2-methyl-4-cyanoquinoline (XVIII), white needles, m. 106.degree., and
adding the Grignard reagent from 12 g. PhBr and 2 g. Mg in 30 mL. Et₂O to
5 g. XVIII in 50 mL. Et₂O; XVII is reduced by (iso-PrO)3Al to
phenyl(2-methyl-4-quinolyl)carbinol, colorless prisms, m. 167.degree.
(from dil. alc.) [acetate (ester), m. 103.degree. (from dil. alc.)], and
by Raney Ni hydrogenation at 100.degree. and 70 atm. to
phenyl(2-methyl-1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 162.degree.
(from dil. alc.), b0.001 130.degree. [N,O-Bz deriv., m. 149.degree. (from
ligroine)]. Raney Ni redn. at room pressure and temp. of
8-benzoylquinoline gives at once phenyl(1,2,3,4-tetrahydro-8-
quinolyl)carbinol, oil, b0.001 120.degree. [1-ON deriv., yellow prisms, m.
146.degree. (from alc.), (di-Bz deriv., m. 132.degree. (from ligroine))].
Nitration of 6 g. VI in 25 mL. concd. H₂SO₄ with 1 mL. nitrating mixt. (=
0.255 g. HNO₃) added at -10.degree., followed by cooling with ice,
filtering, neutralizing with NH₄OH, and crystg. in alc., gives
6-(m-nitrobenzoyl)quinoline, yellow needles, m. 160.degree., which reduced
by SnCl₂ in alc. to the amino compd., yellow crystals, m. 142.degree.
(from H₂O). Similarly, VII is nitrated to 6-(m-nitrobenzoyl)-8-
methylquinoline, m. 156.degree., which is reduced to the 3-amino compd.,
yellow crystals, m. 187.degree. (from ligroine). The

(dichlorobenzoyl)quinolines cannot be nitrated.
IT 858473-25-3P, 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-.alpha.-phenyl-, benzoate 858473-28-6P, 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-2-methyl-.alpha.-phenyl-, benzoate
RL: PREP (Preparation)
(prepn. of)
RN 858473-25-3 CAPLUS
CN 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-.alpha.-phenyl-, benzoate (5CI) (CA INDEX NAME)



RN 858473-28-6 CAPLUS
CN 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-2-methyl-.alpha.-phenyl-, benzoate (5CI) (CA INDEX NAME)

